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Photoisomerization of Stilbene Dendrimers: The Need for a Volume-conserving Isomerization Mechanism[¶]

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ABSTRACT

Highly branched stilbene dendrimers were synthesized and their photochemical behavior was studied. Even the stilbene dendrimer with molecular weight over 6500 underwent *transcis* isomerization in the excited singlet state within the lifetime of 10 ns. The photoisomerization of C=C double bond of stilbene dendrimers in the excited state may proceed by a volume-conserving novel mechanism such as hula-twist rather than conventional 180° rotation around the C=C double bond based on fluorescence and isomerization experiments.

INTRODUCTION

The photoisomerization of C=C double bond is the basic subject of photochemistry (1–7). The photochemical *cis-trans* isomerization of arylethenes usually takes place in the excited state through the rotation around the C=C double bond. We have prepared a series of arylethenes and found that their photochemical isomerization can be modified by introduction of an appropriate aryl substituent on ethylenic carbon inducing the diabatic mutual isomerization and the adiabatic one-way *cis-trans* isomerization depending on the energetic profiles of the aryl substituent (7).

Photoirradiation of simple olefins such as stilbene resulted in mutual isomerization between *cis* and *trans* isomers both in the excited singlet state and in the triplet state decaying at the perpendicular excited state (3,6). In this case, the isomerization is explained by the 180° rotation around the C=C double bond. When the polyaromatic hydrocarbon ring is introduced on the carbon atom of the C=C bond, the mode of photoisomerization changes to result in one-way *cis*-to-*trans* isomerization as observed in 2-styrylanthracene (7).

Intramolecular hydrogen bonding also affected the isomerization behavior (8–19). Thus, 2'-hydroxychalcone underwent one-way

Abbreviations: H-T, hula-twist; THF, tetrahydrofuran.

 $cis \rightarrow trans$ isomerization through intramolecular hydrogen atom transfer in the excited triplet state (8–11). Furthermore, 1-(2-pyridyl)-2-(2-pyrroly)ethene underwent one-way $trans \rightarrow cis$ isomerization in the excited singlet state due to the ultra fast deactivation from the excited state by way of intramolecular hydrogen bonding (12). The *cis* isomer underwent intramolecular hydrogen atom transfer in the excited singlet state as revealed by the observation of the fluorescence spectra at a considerably longer wavelength region with large Stokes-shift. Thus, the aryl group and the hydrogen bonding affected the mode of isomerization (7–20). All these compounds are expected to undergo isomerization around the C=C double bond by 180° rotation.

Photoisomerization is also related to photobiological phenomena such as vision. Rhodopsin is a chromoprotein which accepts light energy and triggers its information, where the primary process is the isomerization around the C=C double bond of retinal chromophore through the excited singlet state (21,22). The primary process is the highly selective 11-*cis* to all *trans* isomerization of the retinal chromophore. The origin of this selectivity and the reaction dynamics after the ultrafast *cis*-*trans* isomerization of the retinal chromophore in the excited singlet state has been explored by ultrafast transient spectroscopy and the low temperature experiments as well as comprehensive studies with model compounds. Thus, the efficiency and the course of *cis*-*trans* isomerization can be controlled by environmental factors such as protein surroundings.

We are interested in the isomerization of artificial polyfunctional photochromic systems in largely congested environments (23,24), especially the effect of substituent of large molecular weight with highly congested chromophore from the point of view of the possibility of searching a novel isomerization mechanism. Therefore, we have studied photoisomerization and excited behavior of stilbene dendrimers.

Dendrimers are well-defined, highly branched macromolecules which have uniform molecular weight. They contain a unique three-dimensional shape with nanoscale size depending on the number of generations and the interior functionality (25–27). Dendrimer chemistry is rapidly expanding in both basic and application studies. When a dendrimer contains a photoreactive

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Scheme 1. Structure of stilbene dendrimers 1-4.

unit as a core, the photochemical properties of the core may be modified by the dendritic branches (28-31).

Only a limited number of photochemical reactions for structural change of dendritic compounds has been reported. Dendrimers having azobenzene as a core have been studied, where *trans*-azobenzene dendrimers underwent isomerization to give the *cis*-isomer on photoirradiation followed by the thermal reverse *cis*-to-*trans* isomerization (32–38). McGrath *et al.* mentioned that they can construct a new photoswitchable dendrimer (32–35). These dendrimers can possibly change size, reactivity, and properties and may open up new potential for application. Aida *et al.* found the antenna effect of the dendrimer to absorb infrared light and reserve the energy to accelerate thermal *cis*-to-*trans* isomerization of azobenzene core (38). Thus, dendrimers have the potential of light harvesting antenna as well as a new material.

The *cis-trans* isomerization can occur through either the inversion mechanism or the rotation mechanism in azobenzene derivatives (39). Because azobenzene does not fluoresce, the dynamic behaviors in the excited state could not be studied.

Our interest to explore the *cis-trans* isomerization of dendritic macromolecules is mainly concerned with the mechanism of isomerization in the excited state (23,24). The photoisomerization of C=C double bond usually takes place by the rotation around the double bond (1–7). We wish to report here the synthesis of a series of stilbene dendrimers **1–4** (Scheme 1) and their photoisomerization behavior. A preliminary result has already been reported (23). The stilbene dendrimers exhibited fluorescence emission with moderately high quantum efficiency. In addition, the *trans* \rightarrow *cis* isomerization may proceed not by the usual one-bond rotation of the double bond but by volume-conserving mechanisms such as twisting of the carbon with the help of the adjacent single bond.

MATERIALS AND METHODS

Syntheses and characterization of the stilbene dendrimers. A series of dendrimers (1–4) was prepared by the convergent method to couple corresponding dendrons with 3,3',5,5'-tetrahydroxystilbene in the presence of potassium carbonate in 2-butanone (40,41) (Scheme 2), and their structures were determined by NMR and MALDI-TOF-MS spectroscopy (23). The



Scheme 2. Synthetic procedures.

purification of stilbene dendrimers was performed by HPLC (Jasco PU-975 and PU-986) equipped with GPC column (Toso TSKgel G2500H_{HR}) eluting with chloroform, and the purity of the dendrimers was checked by HPLC (Jasco PU-980 and MD-915) equipped with GPC column (Toso TSKgel G2500H_{XL}) eluting with tetrahydrofuran (THF).

3,5-Dimethoxybenzyltriphenylphosphonium bromide. A solution of 3,5-dimethoxybenzyl bromide (4.15 g, 17.9 mmol) and triphenylphosphine (4.73 g, 17.9 mmol) in benzene (60 mL) was heated under reflux for 6 h. After conventional workup, the desired product (white powder, yield 7.03 g, 80%) was obtained.

3,3',5,5'-Tetramethoxystilbene (42). At 0°C, 2.66 M n-butyllithium in hexane (1.9 mL, 4.84 mmol) was added to 3,5-dimethoxybenzyltriphenylphosphonium bromide (2.00 g, 4.84 mmol) in THF (30 mL) under argon atmosphere and then the mixture was stirred for 2 h. 3.5-Dimethoxybenzaldehyde (830 mg, 4.84 mmol) in THF (10 mL) was added, and the solution was stirred for 12 h at room temperature. Conventional workup and purification by silica-gel column chromatography (eluent: hexane-ethylacetate = 10:1) gave 399 mg (28%) of *trans* isomer and 662 mg (46%) of cis isomer of 3,3',5,5'-tetramethoxystilbene. trans isomer: white needle; mp141–144°C. ¹H-NMR (200 MHz, CDCl₃) δ 3.83, (12H, s, OCH₃), 6.40 ¹³C-(2H, s, Ph-4), 6.67 (4H, s, Ph-2, 6), 7.01 (2H, s, --CH=CH--) ppm; NMR (50 MHz, CDCl₃) δ 55.34, 100.17, 104.69, 129.27, 139.62, 161.10 ppm. cis isomer: ¹H-NMR (400 MHz, CDCl₃) δ 3.66 (12H, s, OCH₃), 6.31 (2H, t, J = 2.2 Hz, Ph-4), 6.44 (4H, d, J = 2.2 Hz, Ph-2, 6), 6.53 (2H, s,

trans-3,3',5,5'-Tetrahydroxystilbene (43). Boron tribromide (1.25 g, 5.0 mmol) in dichloromethane (5 mL) was added to 3,3',5,5'-tetramethoxy-stilbene (285 mg, 0.95 mmol) in dichloromethane (30 mL) at 0°C and the reaction mixture was stirred at room temperature. After 6 h, 20 mL of water was poured slowly into the reaction mixture, and then 200 mL of water was added. Conventional workup and purification by silica-gel column chromatography (eluent: ethylacetate) gave 230 mg (99%) of 3,3',5,5'-

tetrahydroxystilbene. ¹H-NMR (200 MHz, CD₃OD) δ 6.18 (2H, s, Ph-4) 6.45 (4H, s, Ph-2, 6) 6.86 (2H, s, –CH=CH–).

cis-3,3',5,5'-*Tetrahydroxystilbene*. Boron tribromide (1.25 g, 5.0 mmol) in dichloromethane (5 mL) was added to 3,3',5,5'-tetramethoxystilbene (300 mg, 1.0 mmol) in dichloromethane (30 mL) at 0°C and the reaction mixture was stirred at room temperature. After 48 h, 20 mL of water was poured slowly into the reaction mixture, and then 200 mL of water was added. Conventional workup and purification by silica-gel column chromatography (eluent: ethylacetate) gave 144 mg (59%) of 3,3',5,5'-tetrahydroxystilbene. ¹H-NMR (400 MHz, CD₃OD) δ 6.21 (2H, s, Ph-4) 6.48 (4H, s, Ph-2, 6) 6.89 (2H, s, -CH=CH--).

[*G2*]-*OH* (40). Benzylbromide (50.0 g, 292.3 mmol), 3,5-dihydroxybenzyl alcohol (15.2 g, 146.1 mmol), 18-crown-6-ether (7.72 g, 29.2 mmol) and potassium carbonate (80 g, 578.6 mmol) were suspended in 2.0 L of 2-butanone under nitrogen atmosphere. The mixture was heated under reflux for 60 h. Upon completion of the reaction, the solvent was evaporated and the water (500 mL) and dichloromethane (200 mL) were added to the residue. Conventional workup and purification by silica-gel column chromatography (eluent: hexane–dichloromethane = 9:1) yielded 14.0 g of [G2]-OH (60%) as a white needle. ¹H-NMR (200 MHz, CDCl₃) δ 4.64 (2H, s, CH₂OH), 5.05 (4H, s, CH₂OPh), 6.56 (1H, t, J = 2.2 Hz, *o*-H in Ph), 6.64 (2H, d, J = 2.2 Hz, *o*-H in Ph), 7.35–7.42 (10H, m, Ph') pm; ¹³C-NMR (50 MHz, CDCl₃) δ 65.45, 70.09, 101.6, 105.80, 127.60, 128.08, 128.68, 136.90, 143.85, 160.03 ppm.

[*G2*]-*Br* (40). [G2]-OH (13.6 g, 42.3 mmol) was converted to [G2]-Br by treatment with CBr₄ (17.6 g, 53.1 mmol) and triphenylphosphine (13.9 g, 53.1 mmol) in THF (85 ml) for 15 min at room temperature. Conventional workup and purification with silica-gel column chromatography (eluent: chloroform) gave 5.04 g of [G2]-Br (31%) as a white needle. ¹H-NMR (200 MHz, CDCl₃) δ 4.42 (2H, s, CH₂OH) 5.03 (4H, s, CH₂OPh) 6.55 (1H, t, J = 2.2 Hz, *o*-H in Ph) 6.65 (2H, d, J = 2.2 Hz, *o*-H in Ph) 7.35–7.44 (10H, m, Ph') ppm; ¹³C-NMR (50 MHz, CDCl₃) δ 33.84, 70.04, 102.23, 108.24, 127.63, 128.14, 128.69, 136.63, 139.98, 160.02 ppm.

[G3]-OH (40). [G2]-Br (4.0 g, 10.4 mmol), 3,5-dihydroxybenzyl alcohol (543 mg, 5.22 mmol), 18-crown-6-ether (552 mg, 2.09 mmol) and K₂CO₃ (4.3 g, 31.1 mmol) were suspended in 110 mL of 2-butanone under nitrogen atmosphere and the mixture was heated under reflux for 48 h. Upon completion of the reaction, the solvent was evaporated and the water (80 mL) and dichloromethane (80 mL) were added to the residue. Conventional workup and purification by silica-gel column chromatography (eluent: chloroform) yielded 2.72 g of [G3]-OH (70%) as a colorless glass. ¹H-NMR (200 MHz, CDCl₃) δ 4.62 (2H, d, J = 6 Hz, CH₂OH) 4.97 (4H, s, CH₂OPh) 5.03 (8H, s, CH₂OPh') 6.52 (1H, t, J = 2.2 Hz, *p*-H in inner Ph) 6.67 (2H, t, J = 2.2 Hz, *o*-H in mid Ph) 7.31–7.43 (20H, m, other Ph) ppm. ¹³C-NMR (50 MHz, CDCl₃) δ 65.55, 70.10, 70.12, 101.6, 101.82, 105.95, 128.08, 106.34, 125.75, 127.74, 127.86, 128.05, 128.17, 128.74, 160.05 ppm.

[G3]-Br (40). [G3]-OH (2.72 g, 3.65 mmol) was converted to [G3]-Br by treatment with CBr₄ (17.6 g, 53.1 mmol) and triphenylphosphine (13.9 g, 53.1 mmol) in THF (85 mL) for 20 min at room temperature. Conventional workup and purification by silica-gel column chromatography (eluent: chloroform) gave 1.25 g of [G3]-Br (42%) as a colorless glass. ¹H-NMR (200 MHz, CDCl₃) δ 4.40 (2H, s, CH₂OH) 4.95 (4H, s, CH₂OPh) 5.03 (8H, s, CH₂OPh') 6.51 (1H, t, J = 2.2 Hz, *p*-H in miner Ph) 6.67 (2H, t, J = 2.2 Hz, *p*-H in miner Ph) 6.61 (2H, d, J = 2.2 Hz, *p*-H in mid Ph) 7.30–7.43 (20H, m, other Ph) ppm.

[*G4*]-*OH* (40). [G3]-Br (5.0 g, 6.19 mmol), 3,5-dihydroxybenzyl alcohol (522 mg, 5.10 mmol), 18-crown-6-ether (164 mg, 0.62 mmol) and K₂CO₃ (1.1 g, 8.0 mmol) were suspended in 100 mL of 2-butanone under nitrogen atmosphere, and the mixture was heated under reflux for 48 h. Conventional workup and purification by silica-gel column chromatography (eluent chloroform) yielded 4.5 g of [G4]-OH (91%) as a colorless glass. ¹H-NMR (200 MHz, CDCl₃) δ 4.55 (2H, d, J = 6 Hz, Ph--CH₂OH) 4.94 (12H, s, CH₂O--Ph) 4.99 (16H, s, CH₂O--Ph') 6.53–6.67 (21H, m, Ph') 7.28–7.41 (40H, m, Ph') ppm.

[G4]-Br (40). [G4]-OH (4.5 g, 2.83 mmol) was converted to [G4]-Br by treatment with CBr₄ (1.42 g, 4.27 mmol) and triphenylphosphine (1.20 g, 4.53 mmol) in THF (85 mL) for 20 min at room temperature. Conventional workup and purification by silica-gel column chromatography (eluent: chloroform-hexane = 5:1) gave 1.17 g of [G2]-Br (25%) as a colorless glass. ¹H-NMR (200 MHz, CDCl₃) δ 4.36 (2H, s, CH₂Br) 4.95 (12H, s, CH₂O—Ph) 5.00 (16H, s, CH₂O—Ph') 6.53–6.67 (21H, m, Ph'). *trans-I*. Benzylbromide (674 mg, 3.94 mmol), 3,3',5,5'-tetrahydroxy-

stilbene (200 mg, 0.82 mmol), 18-crown-6-ether (87 mg, 0.33 mmol) and K_2CO_3 were reacted in 2-butanone (40 mL) under nitrogen atmosphere and the mixture was refluxed for 48 h. Conventional workup and purification by silica-gel column chromatography (eluent chloroform) gave 322 mg of *trans*-1 (65%) as a white powder; mp 125–126°C. ¹H-NMR (200 MHz, CDCl₃) δ 5.07 (8H, s, OCH₂Ph) 6.56 (2H, s, stilbene-4,4'), 6.75 (4H, s, stilbene-1,1',5,5'), 6.98 (2H, s, olefin), 7.27–7.46 (20H, m, Ph) ppm. ¹³C-NMR (50 MHz, CDCl₃) δ 70.16, 101.77, 105.95, 121.05, 127.62, 128.10, 128.69, 136.92, 139.27, 160.26 ppm.

cis-1. THF solution of *trans-***1** (73.7 mg in 50 mL THF) was irradiated with 366 nm light of high pressure mercury lamp for 8 h at room temperature. The isomer ratio ([t]/[c]) of the reaction mixture was 1/2. The reaction mixture was concentrated *in vacuo*. Conventional workup and purification by column chromatography provided 16.8 mg of *cis-***1**. ¹H-NMR (400 MHz, CDCl₃) δ 4.88 (8H, s, OCH₂Ph) 6.48 (2H, t, J=2.4 Hz, stilbene-4,4'), 6.51 (2H, s, olefin), 6.55 (4H, d, J=2.4 Hz, stilbene-1,1',5,5'), 7.28–7.35 (20H, m, Ph) ppm.

trans-2. [G2]-Br (1.51 g, 3.94 mmol), 3,3',5,5'-tetrahydroxystilbene (200 mg, 0.82 mmol), 18-crown-6-ether (87 mg, 0.33 mmol) and K₂CO₃ (580 mg, 4.1 mmol) were reacted in 2-butanone (40 mL) under nitrogen atmosphere and the mixture was refluxed for 48 h. Conventional workup and purification by silica-gel column chromatography (eluent: chloroform) gave 782 mg of *trans-2* (65%) as a white powder; mp 146–147°C. MALDI-TOFMS Found: m/z 1476.5. Calcd for C₉₈H₈₄O₁₂Na: [M+Na]⁺, 1476.7. ¹H-NMR (200 MHz, CDCl₃) δ 4.99 (4H, s, CH₂O–St) 5.02 (4H, s, CH₂OPh) 6.56–6.75 (18H, m, Ph) 6.98 (2H, s, olefin) 7.21–7.43 (40H, m, Ph').

trans-3. [G3]-Br (800 mg, 0.99 mmol), 3,3',5,5'-tetrahydroxystilbene (53 mg, 0.22 mmol), 18-crown-6-ether (23 mg, 0.09 mmol) and K₂CO₃ (170 mg, 1.2 mmol) were reacted in 2-butanone (30 mL) under nitrogen atmosphere and the mixture was refluxed for 48 h. Conventional workup and purification by silica-gel column chromatography (eluent: chloroform) gave 782 mg of *trans-3* (82%) as a colorless glass. MALDI-TOFMS Found: m/z 3175.1. Calcd for C₂₁₀H₁₈₀O₂₈Na: [M+Na]⁺, 3174.7. ¹H-NMR (200 MHz, CDCl₃) δ 5.07 (56H, m; OCH₂Ph) 6.45–6.73 (42H, m; Ph) 6.97 (2H, s; olefin) 7.22–7.38 (80H, m; Ph) ppm. ¹³C-NMR (50 MHz, CDCl₃) δ 70.08, 101.90, 106.15, 127.64, 128.08, 128.66, 136.76, 139.49, 160.45 ppm.

trans-4. [G4]-Br (1.15 g, 0.69 mmol), *trans-3,3',5,5'*-tetrahydroxystilbene (40 mg, 0.16 mmol), 18-crown-6-ether (22 mg, 0.08 mmol) and K₂CO₃ (230 mg, 1.2 mmol) were reacted in 2-butanone (35 mL) under nitrogen atmosphere and the mixture was refluxed for 48 h. Conventional workup and purification by silica-gel column chromatography (eluent: chloroform-hexane = 4:1) gave 427 mg of *trans-4* (40%) as a colorless glass. MALDI-TOFMS Found: m/z 6557.8. Calcd for C₄₃₄H₃₇₂O₆₀Li: [M+Li]⁺, 6554.7. ¹H-NMR (400 MHz, CDCl₃) δ 4.82–4.89 (56H, m, OCH₂Ph), 4.91–4.93 (64H, m, OCH₂Ph), 6.43–6.56 (28H, m, Ph), 6.91 (2H, s, olefin), 6.58–6.54 (56H, m, Ph), 7.25–7.36 (160H, m, Ph) ppm.

cis-4. [G4]-Br (2.36 g, 1.42 mmol), *cis*-3,3',5,5'-tetrahydroxystilbene (84 mg, 3.44 mmol), 18-crown-6-ether (19 mg, 0.07 mmol) and K_2CO_3 (118.8 mg, 0.86 mmol) were reacted in 2-butanone (50 mL) under nitrogen atmosphere and the mixture was refluxed for 34 h. Conventional workup and purification by silica-gel column chromatography (eluent: chloroform-hexane = 4:1) gave 854 mg of *cis*-4 (38%) as a colorless glass. ¹H-NMR (400 MHz, CDCl₃) δ 4.79–4.85 (56H, m, OCH₂Ph), 4.86–4.94 (64H, m, OCH₂Ph), 6.48–6.55 (30H, m, Ph), 6.56–6.60 (56H, m, Ph), 7.26–7.31 (160H, m, Ph) ppm.

Absorption and fluorescence spectra and fluorescence lifetime. Absorption and fluorescence spectra were measured on a Shimadzu UV-1600 and on a Hitachi F-4000 fluorescence spectrometer, respectively. Fluorescence lifetimes were determined with Horiba NAES-1100 time resolved spectrofluorometer.

Quantum yield of fluorescence emission. Quantum yield of fluorescence emission were determined by using naphthalene ($\Phi_f = 0.23$) (44) and anthracene ($\Phi_f = 0.27$) (44) as standards. A correction of the difference in refractive index among the solvents was made for each sample. The absorbance of the sample solution at the excitation wavelength was adjusted to less than 0.1, and the integration of the fluorescence spectra over wave number was plotted against absorbance at excitation wavelength. The slope of these plots gives the relative value of the fluorescence quantum yield, and the quantum yield of fluorescence emission was determined.

Quantum yield of isomerization. Quantum yield of trans \rightarrow cis isomerization ($\Phi_{t\rightarrow c}$) of trans-1 was determined on irradiation at 313 nm from a 150 W xenon lamp through a monochrometer. The sample solution was dearated by bubbling argon and irradiated for 3 min to keep the conversion within 5%. Light intensity was determined by tris(oxalato)-



Figure 1. Absorption spectra of stilbene dendrimers in THF solution.

ferrate(III) actinometry (45). The concentration of each isomer was determined by high performance liquid chromatography through a column (Toso CN-80Ts) eluting with hexane–ethyl acetate = 9:1. The quantum yield of *trans* \rightarrow *cis* isomerization for *trans*-2–4 was determined by comparison of the rate of absorbance change of the optically matched solution at 313 nm with that of *trans*-1 under the same irradiation conditions.

Laser flash photolyses. Laser flash photolyses were performed by using an excimer laser (Lambda Physik LPX-100, 308 nm, 20 ns fwhm) as an excitation light source and a pulsed xenon arc (Ushio UXL-159) was used as a monitoring light source. A photomultiplier (Hamamatsu R-928) and a storage oscilloscope (Iwatsu TS-8123) were used for the detection.

RESULTS

Absorption spectra

Figure 1a showed the absorption spectra of *trans*-**1**-**4** in THF at room temperature. All compounds exhibited similar absorption spectra at 300–360 nm with the absorption maximum at 310 nm due to the stilbene core. However, the absorbance at 280 nm increased with increasing of the generation of the dendrimer due to the absorption of the benzyl ether group of the surrounding dendron. The absorption profile at 300–360 nm is almost the same for *trans*-**1**-**4**, indicating that the peripheral dendron group does not influence the electronic properties of stilbene dendrimers.

Figure 1b also showed the absorption spectra of *cis*-1 and *cis*-4 in THF. The absorbance at 280 nm mostly due to the benzyl ether dendron is almost the same between *cis* and *trans* isomers. However, the absorption coefficient of *cis* isomers at longer wavelength regions at 300–360 nm is considerably smaller than that of *trans* isomers by a factor of 3–4. Thus, the absorption property of stilbene core is not influenced by the substitution of benzyl ether–type dendron.

Fluorescence spectra

The fluorescence emission has been observed for all the stilbene dendrimers *trans*-**1**-**4** with similar fluorescence maximum at 380 nm (Fig. 2) in THF. The quantum yield of fluorescence emission in THF was determined by using naphthalene ($\Phi_f = 0.23$) (44) and anthracene ($\Phi_f = 0.27$) (44) as standards. The emission spectra of



Figure 2. Fluorescence (solid line, $\lambda_{ex} = 310$ nm) and fluorescence excitation spectra (dashed line, $\lambda_{em} = 375$ nm) of stilbene dendrimers in THF solution at room temperature under argon atmosphere: (a) *trans-1*, (b) *trans-2*, (c) *trans-3*, (d) *trans-4*.

the sample solution were measured with changing the absorbance of the excitation wavelength (310 nm) from 0.05–0.1, and the integration of the spectra was done by converting the wavelength to wave number. The integrated values are plotted against the absorbance of the excitation wavelength. Thus, the slope is the relative value of the fluorescence quantum yields among the measured values with different concentrations and different samples, and the quantum yield of fluorescence emission can be derived. The quantum yield of fluorescence emission is almost the same for *trans*-1–4 with the value of *ca* 0.43 \pm 0.02 on 308 nm irradiation (note that the previously reported value (23), 0.55, 0.58, 0.58 and 0.71 for *trans*-1, -2, -3 and -4, were wrong).

The fluorescence excitation spectra are similar to the absorption spectra of the corresponding dendrimers (Fig. 2). These results indicate that not only the photon absorbed by stilbene core but also that absorbed by surrounding dendron groups could induce the fluorescence emission from the stilbene core. The relative intensity of the fluorescence excitation spectrum at 280 nm becomes smaller compared with the absorption spectra in higher generation. Therefore, the energy transfer efficiency from the peripheral dendron group to the core stilbene decreased with increasing the generation, which is the increasing size of the dendrimer. Because the surrounding dendron and the stilbene core have no π conjugation, one could explain the occurrence of the efficient energy transfer from the dendron group to the stilbene core by dipole-dipole interaction to give the core fluorescence emission. The efficiency of the energy transfer process from dendron group to the core (Φ_{ET}) was estimated by comparing the fluorescence



Figure 3. Time dependence of the absorption change observed on 330 nm light irradiation in THF at room temperature under argon atmosphere.

quantum yield by excitation at 280 nm (dendron excitation) with that by excitation at 310 nm (core stilbene excitation). Thus, Φ_{ET} was determined to be 0.81 and 0.34, respectively, for *trans*-**3** and -**4**. The energy transfer efficiency decreased with increasing generation of the dendrimers. These results indicate the occurrence of Förster type of energy transfer.

Photoisomerization

On irradiation with 330 nm light from the 150 W xenon lamp through the monochrometer, *trans* isomers of **1–4** underwent *trans*to-*cis* isomerization as revealed by the change of the absorption spectra in THF. Figure 3 shows the time profile of the change of absorbance at 330 nm for *trans*-**1–4**. The initial absorbance of *ca* 0.1 at 330 nm decreased with irradiation time to give constant value of *ca* 0.02 for all dendrimers indicating the higher *cis* isomer composition at the photostationary state on 330 nm irradiation.

The isomer ratio at the photostationary state was determined starting from both pure *cis* and *trans* isomers. Thus, pure *cis*-4 and *trans*-4 gave the isomer mixture of [t]/[c] = 5/95 exhibiting almost one-way photoisomerization from *trans*-to-*cis* direction on 330 nm irradiation as shown in Fig. 4. However, *cis*-1 did not give *trans*-1 but may undergo cyclization reaction to give dihydrophenanthrene type compounds as revealed by the observation of *the absorption* change. The details of *cis*-*trans* isomerization of *cis*-1 will be reported elsewhere.

The quantum yields of *trans* \rightarrow *cis* photoisomerization ($\Phi_{t\rightarrow c}$) have been determined on irradiation with 313 nm light. The value of $\Phi_{t\rightarrow c}$ was 0.32, 0.32 and 0.29 for *trans*-1, -2 and -3, respectively. The $\Phi_{t\rightarrow c}$ was 0.24 for *trans*-4. Therefore, the efficiency of *trans*-to-*cis* isomerization is almost the same among *trans*-1–3, but the value for *trans*-4 is considerably smaller than *trans*-1–3. The introduction of peripheral large dendrons may suppress the photoisomerization efficiency.

The observation of the considerably high *cis* isomer composition at the photostationary state indicates the inefficient $cis \rightarrow trans$ isomerization through the excited state. Usually the isomer composition at the photostationary state can be described by

$$([t]/[c])_{\text{pss}} = (\epsilon_c/\epsilon_t)(\Phi_{c\to t}/\Phi_{t\to c})$$

The absorption coefficient of *cis* and *trans*-**4** is 7400 and 26400, respectively, at 330 nm and $\Phi_{t\rightarrow c}$ was determined to be 0.24. Therefore, from the observed $([t]/[c])_{pss} = 5/95$ and the above values, one can estimate the quantum yield of isomerization from *cis*-to-*trans* to be as small as 0.05. The small value indicates the efficient deactivation processes from the excited singlet state of *cis* isomers other than *cis*-*trans* isomerization.



Figure 4. Absorption spectra of *cis*- and *trans*-4 and the isomer mixture at the photostationary state on irradiation with 330 nm light in THF at room temperature under argon atmosphere.

Fluorescence lifetime

Stilbene dendrimers *trans*-**1**-**4** have a fluorescence lifetime of 9.3-9.7 ns at 23° C, and the lifetime changed with the temperature to give 10.8-11.3 ns at 0° C and 7.7-8.0 ns at 50° C in THF. The decay curves and the determined lifetimes are summarized in Fig. 5. The observation of the temperature effect on the fluorescence lifetime indicates that the decay processes involve the deactivation process for activation energy. Usually *trans*-olefins deactivate from the excited singlet state by three processes: intersystem crossing to the triplet state, fluorescence emission and *trans*-*cis* isomerization. In these deactivation processes, only the *trans*-*cis* isomerization is expected to suffer from the temperature effect, where *trans*-*cis* isomerization is uppressed at lower temperature, resulting in the decrease of the deactivation rate constant and increase of the singlet lifetime. Thus, *cis*-*trans* isomerization of **1**-**4** should take place in the excited singlet state.

The fluorescence lifetimes of *trans*-1-4 under oxygen atmosphere are smaller than those under argon atmosphere (Fig. 6). Thus, the singlet lifetime is 3.2, 3.5, 4.1 and 5.2 ns for *trans*-1, -2, -3 and -4, respectively, under oxygen. Although the fluorescence lifetime under argon is almost the same among *trans*-1-4, the fluorescence lifetime under oxygen is slightly different depending on the generation of the dendrimer. The higher generation dendrimer suffered less from oxygen quenching than that of lower generation dendrimer, and the quenching rate constant was determined to be 2.3, 2.0, 1.6 and $0.9 \times 10^{10} M^{-1} s^{-1}$, respectively, for *trans*-1, -2, -3 and -4.

Effect of temperature and viscosity on trans-cis isomerization

The absorbance change at 330 nm on irradiation at 330 nm in THF was measured at 5°C, 22°C and 40°C. The rate of the absorbance decrease increases with increasing temperature and generation. The relative rate of isomerization was determined from the initial slope in Fig. 7. These results indicate that the isomerization on direct irradiation should take place in the singlet excited state, and the isomerization efficiency may decrease with the substitution of the large peripheral dendron in *trans*-4. The *cis* isomer composition at the photostationary state is slightly higher for *trans*-2 than *trans*-4, indicating that the *trans*-to-*cis* isomerization was suppressed by the peripheral dendron group in *trans*-4 rather than *cis*-to-*trans* isomerization.

The quantum yield of $trans \rightarrow cis$ isomerization decreased with temperature from 0.45 at 40°C to 0.32 at 22°C and 0.20 at 5°C for *trans*-2 and from 0.30 at 40°C to 0.24 at 22°C and 0.18 at 5°C for *trans*-4. Thus, the efficiency of isomerization and the temperature



Figure 5. Temperature effect on the fluorescence decay curve in THF under argon atmosphere: (a) *trans*-1, (b) *trans*-2, (c) *trans*-3, (d) *trans*-4.

effect on the isomerization quantum yield are similar for *trans-***2** and *trans-***4**, indicating that the isomerization of the C=C double bond in the excited singlet state was scarcely affected by the large substituent.

The rate constant of isomerization in the excited singlet state was estimated by $k_{\rm iso} = (1/\tau_{\rm s}) \times 2\Phi_{\rm t\to c}$. The Arrhenius plot of these values gave the activation energy $E_{\rm a}$ and the frequency factor for *trans* \rightarrow *cis* isomerization deactivating at the perpendicular singlet excited state to be 5.7 kcal mol⁻¹ and $1.1 \times 10^{12} \, {\rm s}^{-1}$ for *trans*-**2** and 6.3 kcal mol⁻¹ and $2.7 \times 10^{12} \, {\rm s}^{-1}$ for *trans*-**4**. These values are almost the same.

The *trans-cis* photoisomerization of *trans-2* and *trans-4* is studied in solvent with different viscosity. The isomerization efficiency at higher viscosity solvent (v = 2.9 cSt, THF:liq. paraffin = 1:1) is slightly lower than that at low viscosity solvent (v = 0.50 cSt, THF:Hexane = 1:1) by at most 10% for both *trans-2* and -4. Thus, solvent viscosity does not severely influence the photoisomerization behavior.

Laser flash photolysis

All the dendrimers *trans*-1–4 gave no detectable T–T absorption spectra indicating that the isomerization proceeds not in the triplet



Figure 6. Effect of oxygen on the fluorescence lifetime of stilbene dendrimers in THF at room temperature under argon atmosphere: (a) *trans*-1, (b) *trans*-2, (c) *trans*-3, (d) *trans*-4.

state but in the excited singlet state. When the sample was irradiated by the focusing laser, one can observe transient spectra, which was not quenched by molecular oxygen. Thus, in these conditions the compounds absorbed multiphoton simultaneously and were photoionized to give cationic radicals. These spectra were shown in Fig. 8. However, no transient assigned to the T–T absorption was observed.

DISCUSSION

As discussed in Results, fluorescence lifetimes are almost the same for *trans*-**1**-**4** at room temperature. In addition, the fluorescence quantum yields are almost the same among the dendrimers. Therefore, the introduction of the large peripheral substituents does not seem to influence the photochemical and photophysical behavior of stilbene dendrimers.

The singlet energy transfer from the peripheral dendron group to the core stilbene took place with the efficiency of 0.81 and 0.34 for *trans*-3 and -4, respectively. Previously, Aida *et al.* reported that the energy transfer from benzyl ether–type dendron group to the core metal porphyrin took place efficiently thereby behaving as an artificial light-harvesting antenna depending on the generation



Figure 7. Time dependence of the absorbance change observed on 330 nm light irradiation in THF at varying temperature under argon atmosphere for *trans*-2 (a) and *trans*-4 (b).

and the shape of the dendrimers (46). For example, in porphyrin dendrimers surrounded by benzyl ether-type dendron, energy transfer from benzyl ether dendron to the core took place by almost 100% efficiency. However, for porphyrin dendrimers where only half of the porphyrin peripheral was surrounded by benzyl ether dendron showed inefficient energy transfer from the dendron to the core. Thus, they suggested that in spherical type of dendrimers, absorbed photons may migrate around the peripheral dendron groups and finally reach the energetically stable porphyrin core without undergoing radiationless deactivation to the ground state. The structure of the dendron is slightly different between the reported porphyrin dendrimers and our compounds. However, even for the spherical type dendrimers, the efficiency of the energy transfer to the core decreased with increasing generation as observed in trans-1-4. The present results in trans-1-4 are in accord with the usual Förster type energy transfer mechanism.

Very interestingly the singlet lifetimes and the temperature effect on the lifetimes were almost the same among *trans*-1–4. Therefore, the peripheral large dendron group seems to exhibit no considerable effect on the *trans* \rightarrow *cis* isomerization of the stilbene core. These results indicate that the photoisomerization of the higher generation stilbene dendrimer takes place not by a conventional 180° rotation around the C=C double bond but by another mechanism with the volume-conserving process.

The deactivation from the excited singlet state of the *trans* isomer usually takes place by fluorescence emission, intersystem crossing to the triplet state and *trans–cis* isomerization. The isomerization through the singlet excited state proceeds by the twisting around the C=C double bond to give the perpendicular singlet excited state followed by the radiationless deactivation to the ground state to give *cis* and *trans* isomers in the ground state. Thus, the twisting process in the excited singlet state seems to be affected by the large substituent at room temperature.

On photoirradiation, *trans*-stilbene undergoes *trans* \rightarrow *cis* isomerization in the excited singlet state to give perpendicular singlet excited state followed by deactivation to the ground state



Figure 8. Transient absorption spectra observed on laser flash photolysis with focused 308 nm laser beam.

perpendicular conformation to give *cis*-stilbene with the quantum yield of 0.50 in addition to the fluorescence emission with the quantum yield of 0.04 (2). On photoirradiation, *cis*-stilbene undergoes cyclization to give dihydrophenanthrene type compounds with the quantum efficiency of 30% followed by reversion to the starting *cis*-stilbene or undergoes isomerization to give the perpendicular singlet state and finally gives *trans*-stilbene with the quantum yield of 0.35. The lifetime of *cis*- and *trans*-stilbene were reported to be 1 and 70 ps, respectively, at room temperature. Thus, the isomerization barrier in the *cis*-to-*trans* and *trans*-to-*cis* isomerization of stilbene in the excited singlet state seems very small and one may expect to observe the effect of largely congested substituents on the photoisomerization mechanism as well as isomerization efficiency around the C=C double bond of stilbene.

As described in Results, the photoisomerization around the double bond of the stilbene core took place relatively efficiently even for the fourth generation dendrimer with molecular weight as high as 6500, indicating a novel mechanism of isomerization of stilbene dendrimers. The temperature effect and the viscosity effect may suggest some interesting mechanism.

The temperature effect on the fluorescence lifetime is almost the same among all dendrimers. When we started this project, we expected the peripheral dendron effect on the photoisomerization behavior of the core stilbene because the isomerization by C=C double bond twisting needs large volume change as well as large molecular structural change according to *trans-cis* isomerization. The above results that large substituents scarcely affect the deactivation process by way of C=C double bond twisting in the excited singlet state indicate the isomerization mechanism other than the usual 180° rotation around the C=C double bond in higher generation dendrimers.

The isomerization of the one-bond rotation around the central double bond needs considerably large volume change in *trans-4*,



Figure 9. Potential energy surfaces of *trans-cis* isomerization by one-bond rotation and H-T mechanism.

which cannot possibly take place within the singlet lifetime. Thus, a volume-conserving model seems to be needed for the isomerization of stilbene dendrimers with these large molecular weights (Scheme 3 and Fig. 9). For cis-trans isomerization in highly condensed media at low temperature or in protein, Liu and Hammond postulated the quite interesting mechanism called Hula-Twist (H-T) mechanism (47–49), where isomerization takes place not by the one-bond rotation around the double bond but by the concomitant twist of the double bond and the adjacent single bond to accomplish the double bond isomerization. Thus, the mechanism can be applied for the isomerization of chromoproteins such as rhodopsin and yellow proteins (50,51). These proteins seem to have a restriction of the double bond rotation. Actually, the H-T mechanism was observed in the isomerization of the vitamin D derivatives at 77 K (52). In addition, the isomerization of olefins with small molecular weight in glassy solvent at 77 K have been proposed to proceed by H-T mechanism (53,54).

The H-T mechanism does not need a large motion of internal rotation, and we may explain the relatively efficient trans-cis photoisomerization in trans-4 by this mechanism. The H-T mechanism may operate easily in cis-to-trans isomerization because the intrinsic energy barrier may be smaller in this direction than trans-to-cis isomerization. We have prepared cis-4 and studied the photoisomerization behavior. On photoirradiation, cis-4 underwent cis-to-trans isomerization in the excited singlet state. The quantum yield of $cis \rightarrow trans$ isomerization was estimated to be as small as 0.05, which is less than a quarter of the quantum yield of *trans* \rightarrow *cis* isomerization. The result seems to indicate the effect of the dendron group on the photoisomerization from the *cis*-to-*trans* direction. Thus, in *cis*-4 the peripheral benzyl ether dendrons substituted at the phenyl ring come close to inducing the steric restriction along the C=C rotation, which is not present in trans-4. In other words, we could expect that cis-4 cannot undergo isomerization around the double bond due to the interaction of the peripheral dendron group to increase the barrier



Scheme 3. Molecular movement along the photoisomerization by H-T mechanism and one-bond rotation.

for rotation and to inhibit the rotation. The result obtained in studies of the quantum yield of *cis*-to-*trans* isomerization to be as low as 0.05 is a compromise of the above two factors, the low energy barrier for facile *cis*-to-*trans* isomerization in the excited singlet state intrinsically present in the stilbene core and the steric effect by the large dendron group to inhibit the isomerization from *cis*-to-*trans* isomerization in the excited singlet state.

There is no example of the isomerization of artificial large molecules that restrict conventional isomerization by the steric effect but can undergo isomerization by an alternative rotational mechanism. The stilbene dendrimers studied here are good models of such chromoproteins. The present finding may indicate that isomerization by the H-T mechanism can occur at room temperature even in fluid solution.

CONCLUSION

A series of stilbene dendrimers exhibited fluorescence emission with considerably high quantum efficiencies. In addition, even the stilbene dendrimer with a molecular weight as high as 6548 (*trans*-4 and *cis*-4) can undergo isomerization around the double bond within the lifetime of its excited singlet state as revealed by fluorescence spectroscopies. The isomerization may proceed not by a one-bond rotation of 180° but by a volume-conserving process such as the H-T mechanism. The present findings may be extended

for the construction of artificial chromoproteins and the model studies of photoresponsive biomolecules by exploring the photochemistry of the photoreversible core and the subsequent moving of the peripheral dendron group.

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